

Low-Temperature, High-Throughput Process for Thin, Large-Grained Poly Si

**Final Technical Report
24 May 1999–25 July 2003**

H.A. Atwater
*California Institute of Technology
Pasadena, California*



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
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Contract No. DE-AC36-99-GO10337

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Table of Contents

Overview of Project	1
Project Goals	1
Project Approach	1
Accomplishments under Project	1
Technical Discussion: Wire Surface Kinetics in Hot-Wire Chemical Vapor Deposition	3
Prior Work	4
Threshold Ionization Mass Spectrometry Data Acquisition	6
Results from Gas Species Detection	7
Wire Characterization	9
References	16
Publications and Subcontract	18

List of Figures

Figure 1. Diagram of the Hot-Wire Chemical Vapor Deposition System	5
Figure 2. Low Pressure (5×10^{-6} Torr) Radical Species Measurements Obtained Using a New W Wire	7
Figure 3. Summary of Experimental Studies on W Wire Surface Kinetics	7
Figure 4. SiH_x Radical Signals Measured from an Aged W Wire at a Total Pressure of 5×10^{-6} Torr	9
Figure 5. Surface Morphology of New (a), Heat-Treated (b), and Aged (c) Wires	10
Figure 6. Scanning Electron Microscopy (SEM) Image of Aged Tungsten Wire	11
Figure 7. Si-W Phase Diagram, Created with TAPP v2.1 (Thermochemical and Physical Properties), ES Microwave, 1991	12
Figure 8. Mass Spectrometry Evidence for Si Incorporation by W Wire	13
Figure 9. Rates of Interest for Wire Surface Kinetic Process	14

List of Tables

Table 1. Composition of Used Tungsten Wire, as Determined by Auger Electron Spectroscopy (AES)	12
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Low-Temperature, High Throughput Process for Thin, Large-Grained Poly Si

Overview of Project

Project Goals:

The overall project goal is to understand the fundamental gas phase, surface and interface science issues relevant to low temperature ($T < 600\text{ }^{\circ}\text{C}$) synthesis of polycrystalline silicon films on low-cost (e.g., glass) substrates. This understanding will be used to delineate the path to break through existing barriers to high-rate synthesis of high-quality thin films for polycrystalline silicon photovoltaics applications. In this context, high quality refers to large grain size ($>$ film thickness) and long ($>$ film thickness) minority carrier diffusion length.

Project Approach:

The approach to high rate synthesis of large-grained films at low temperatures was twofold, consisting of research on

1. **Selective Nucleation and Solid Phase Epitaxy** (SNSPE) growth to form a thin ($< 1\text{ }\mu\text{m}$ thick) large-grained polycrystalline silicon template film from amorphous silicon starting material. The rate of solid phase crystallization is greatly enhanced relative to that for pure amorphous silicon via dopant-enhanced or silicide-enhanced crystallization, enabling large grain structures to be achieved at $< 600\text{ }^{\circ}\text{C}$ in reasonable times.
2. **High Rate Epitaxial Growth By Hot-Wire Chemical Vapor Deposition** (HWCVD) of a thicker ($1\text{-}30\text{ }\mu\text{m}$ thick) layer of silicon on the large-grained polycrystalline silicon template film. Hot-wire chemical vapor deposition is a promising technique for deposition of thin film amorphous, polycrystalline, and epitaxial silicon films for photovoltaic applications. The research on HWCVD was focused on both modeling and simulation of gas phase kinetic processes and film growth. Modeling efforts include quantitative models of gas phase species and reaction kinetics between the wire and substrate using particle-based direct simulation Monte Carlo methods appropriate for low pressure reacting flows, as well as *ab-initio* calculations of the thermochemistry and kinetics of relevant silicon-hydride reactions. Experiments include quadrupole mass spectrometry of gas phase species as well as film growth and characterization by reflection high-energy electron diffraction, transmission electron microscopy, atomic force microscopy and Rutherford backscattering spectrometry.

Accomplishments under Project:

1. **Selective Nucleation and Solid Phase Epitaxy** (SNSPE) growth was used to form thin ($< 1\text{ }\mu\text{m}$ thick) large-grained polycrystalline silicon template films from amorphous silicon starting material. While researching the SNSPE process we
 - Found that the rate of solid phase crystallization can be greatly enhanced relative to that for pure amorphous silicon via dopant-enhanced or silicide-

enhanced crystallization, enabling large grain ($> 100\ \mu\text{m}$) structures to be achieved at $< 600\ ^\circ\text{C}$ in reasonable times.

- Developed inkjet printing of Ni nanoparticles onto Si substrates as a low cost mask-free method for metal-induced nucleation in solid phase crystallization of amorphous Si layers.
- Demonstrated SNSPE growth with low Ni content. Probed Ni content in Ni-mediated crystallized Si template layers and a microns thick epitaxial layer atop the template layer (deposited by molecular beam epitaxy) with x-ray fluorescence microprobe at Advanced Light at Lawrence Berkeley National Laboratories.
- Performed Si epitaxy on SNSPE templates and characterized Ni uptake in the epitaxial Si layers; Ni content was found to be below the SIMS detection limit in epitaxial Si layers except with $< 0.4\ \mu\text{m}$ from the template/epitaxial Si interface.
- Demonstrated SNSPE growth exhibits a synergistic enhancement in growth rate with concurrent Ni and P doping.
- Estimated vacancy depth profile in doped Si films, from positron annihilation spectroscopy and progressive etchback of the film surface, in collaboration with Washington State University.

2. ***High Rate Epitaxial Growth By Hot-Wire Chemical Vapor Deposition***

- Experimentally determined the low-coverage nucleation kinetics of silicon on silicon dioxide substrates.
- The wire-catalyzed silane decomposition process has been studied in detail by use of mass spectrometry. The atomic silicon radical was the predominant formed for wire temperatures above 1500 K, and catalysis was evident for SiH_3 production with the use of a new wire. Aged wires appear to produce radicals by a non-catalyzed route and chemical analysis of these wires reveal large quantities of silicon at the surface, consistent with the presence of a silicide layer.
- Performed quantitative measurements of gas phase radicals, via threshold ionization mass spectrometry, that play a role in the growth of high quality polycrystalline and epitaxial silicon. Threshold ionization mass spectrometry revealed large quantities of the SiH_2 radical, attributed to heterogeneous pyrolysis on the walls of the reactor. At dilute (1%) silane pressures of up to 2 Torr, a negligible amount of ions and silicon agglomerates (Si_2 , Si_2H , Si_2H_6) were detected.

- Developed and applied a two-dimensional direct simulation Monte Carlo modeling of the HWCVD reactor under conditions relevant to high quality polycrystalline and epitaxial silicon.
- Density functional theory calculations reveal an energetically favorable route for the reaction of Si and SiH₄, producing Si₂H₂ and H₂. The trace amounts of Si₂H₂ observed experimentally, however, suggest that an intermediate spin state transition involved in this reaction is slow under the hot-wire conditions used.
- Under conditions where agglomerate formation does not occur, continuum simulations predict a maximum achievable HWCVD growth rate of 10 nm/s for dilute (1%) silane conditions and a rate of 50 nm/s for pure silane.
- Monte Carlo simulations of the hot-wire reactor suggest SiH₃ is the predominant growth species under conditions leading to amorphous and polycrystalline growth. The flux of atomic hydrogen, rather than the identity of the precursor, appears to be the more important factor in governing the amorphous-to-microcrystalline transition that occurs upon hydrogen-dilution.
- A method for in-situ generation of SiH₄ by atomic hydrogen etching was evaluated. Using a cooled crystalline silicon target in an H₂ ambient produced negligible etching, while an amorphous silicon film target was etched at a rate of up to 2.5 nm/min. In the latter case, net deposition at 0.6 nm/min onto a heated Ge(100) substrate resulted. A method for more efficient etching of crystalline silicon materials was proposed.

Technical Discussion: Wire Surface Kinetics in Hot-Wire Chemical Vapor Deposition

In this section, we describe in detail measurements of wire surface kinetics during hot wire chemical vapor deposition. In this work, wire-desorbed radicals present during hot-wire chemical vapor deposition growth were measured by quadrupole mass spectrometry. New wires were found to produce Si as the predominant radical for temperatures above 1500 K, with a minor contribution from SiH₃, consistent with previous measurements; the activation energy for the SiH₃ signal suggests its formation is catalyzed. Aged wires also produce Si as the predominant radical (above 2100 K), but show profoundly different radical desorption kinetics. In particular, the Si signal exhibits a high temperature activation energy consistent with evaporation from liquid silicon. The relative abundance of the other SiH_x species suggests that heterogeneous pyrolysis of SiH₄ on the wire may be occurring to some extent. Chemical analysis of aged wires by Auger Electron Spectroscopy suggests that the aging process is related to the formation of a silicide at the surface, with silicon surface concentrations as high as 15 atomic %. A limited amount (2 atomic %) of silicon is observed in the interior as well, suggesting that diffusion into the wire occurs. Calculation of the relative rates for the various wire kinetic processes, coupled with experimental observations, reveals that silicon diffusion

through the silicide is the slowest process, followed by Si evaporation, with SiH₄ decomposition being the fastest.

Introduction

A knowledge of the primary radicals produced on the wire in a hot-wire chemical vapor deposition (HWCVD) reactor is critical to optimization of film microstructure and quality, as well as for modeling gas-phase chemistry. In the low pressure, collisionless regime, these wire-desorbed radicals may act as the primary film deposition precursors, while at higher pressure, they may react with other species in the gas phase to produce the precursors. In particular, the study by Molenbroek *et al.*¹ suggested a direct correlation between amorphous film quality and the degree of reaction of wire-generated Si in the gas-phase.

Recently, it has been demonstrated that wire age has an effect on the resulting electronic properties of the grown film,² thought to be related to differences in radical chemistries associated with aged versus new wires. No studies have examined, however, what these differences in radical chemistry might be, if they exist.

Prior Work

There have been a number of recent reports³⁻⁶ of the distribution of wire-desorbed radicals, following the early report by Doyle *et al.*⁷ Experiments conducted using similar detection schemes, such as vacuum ultraviolet (VUV) photo-ionization mass spectrometry, have shown quite different results in some cases.^{4,5} Whether these differences are due to the different histories of the wire used or differences in the reactor condition (e.g. amorphous silicon-coated walls) is unclear.

One point that most of these studies agree on is that Si is the dominant radical observed at high wire temperatures (above 1800 K). However, the distributions of the minor species found at lower temperatures are in discrepancy among the various studies. In the report of Doyle *et al.*,⁷ SiH₃ was the next most abundant radical to Si. Duan *et al.*⁵ report disilicon species (Si₂H_x) as the next most abundant, followed by SiH₃; the presence of Si₂H_x was thought to be related to wall reactions, however, and not a result of wire processes. Tange *et al.*⁴ report SiH₂ as the next most abundant radical, followed by SiH₃. In contrast to the other studies, the SiH₂ and SiH₃ radicals show a precipitous drop above 1700 K. These discrepancies have motivated a detailed study of radical desorption kinetics under conditions where the wire history (as well as that of the reactor) is well known. Also, a detailed chemical and surface analysis of aged wires has been made to better understand the aging mechanism.

Experimental Approach

Measurements were performed in an ultra-high vacuum chamber with a base pressure of order 10⁻⁹ Torr. Background gases consist mostly of residual H₂ and He. Operating pressures were approximately 5x10⁻⁶ Torr of a dilute (1%) mixture of SiH₄ in He (i.e. SiH₄ partial pressures of 5x10⁻⁸ Torr), at flow rates of less than 1 sccm. These low pressures were chosen in order to eliminate the effects of gas-phase reactions and focus exclusively on wire processes. A straight tungsten wire of 0.5 mm diameter and 12 cm length was used. Although other studies⁴ have examined alternate wire materials (tantalum and molybdenum), tungsten was chosen due to its low vapor pressure across the temperature range of interest. Tungsten is also the most widely used wire material in HWCVD. Figure 1 provides a diagram of this hot-wire reactor.

The wire temperature was determined by using a single wavelength, disappearing filament optical pyrometer (Leeds and Northrup, Model 8622-C), with corrections made for effective emissivity. The emissivity of elemental tungsten was taken as 0.44 (Ref. 8), along with a quartz transmission factor of 0.93, to give an effective value of 0.41. For the temperature dependent radical measurements of the present study, the largest source of error comes from the wire temperature determination (limited by the visual acuity of the user) and is estimated to be approximately ± 50 K over the entire temperature range investigated.

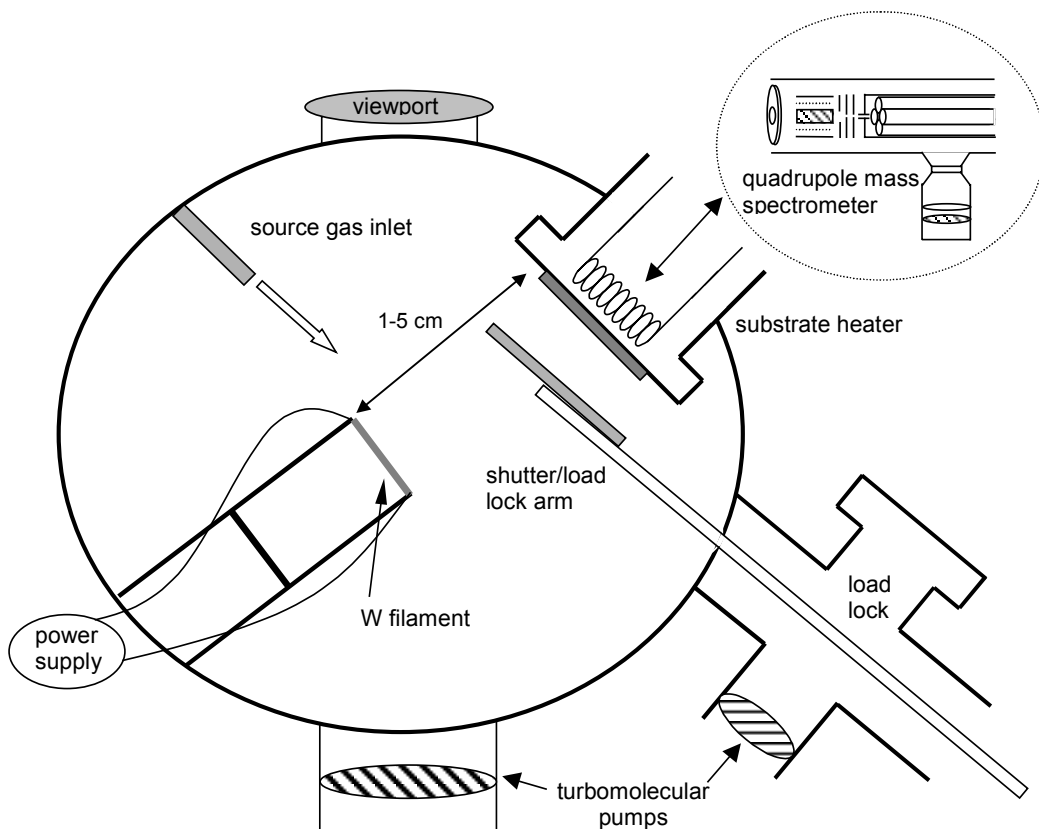


Figure 1. Diagram of the hot-wire chemical vapor deposition system.

Radical measurements were made with the use of a quadrupole mass spectrometer (Hiden Analytical Ltd., HAL RC201), with the capability of tunable electron energy to enable radical detection. The spectrometer is placed at the same location as the substrate heater during film growth, as Figure 1 shows. The radical detection technique used here relies on the lower electron energy for direct radical ionization ($e^- + A \rightarrow A^+ + 2e^-$) versus ion production by dissociation of a parent molecule ($e^- + AB \rightarrow A^+ + B + 2e^-$).⁹ Measurements are made at a fixed electron energy over a range of masses¹⁰. The electron energy chosen for these measurements was 10.5 eV, as it was found to result in preferential ionization of radical species, limiting the extent of dissociative ionization of SiH_4 to produce SiH_x ($x = 0-3$). The choice of energy is critical, as interference from SiH_4 dissociation at high energies can reduce the radical detection sensitivity. In addition, a characteristic of electron impact ionization, in contrast to a process

such as photoionization, is the spread in the energy distribution (estimated to be 0.5 eV full-width half-maximum for our instrument). This spread allows for dissociative ionization of SiH₄ at energies that are nominally below the appearance potential of a particular radical, an effect similar to that previously noted by Hsu *et al.*⁹ We find this effect to be most important for the SiH₃ radical, given that SiH and SiH₂ are only trace in abundance, and that the gap between ionization and appearance potentials is slightly smaller for SiH₃ (3.9 eV) than for Si (4.3 eV).¹¹ A related effect that could potentially bias the measurement of radicals is ion production from vibrationally excited SiH₄, at energies below the nominal appearance potential of the particular ion.¹² As a result of these effects, the data to be presented have been corrected for trace dissociative ionization by a method to be discussed in next section.

Since the chamber used in this study is also used during high-pressure film growth, a thin layer of amorphous silicon is often observed on the walls. In order to eliminate the contribution of etching of this silicon from the walls to the measured radical signals, the chamber was cleaned by introducing H₂ at total pressures in the range of 100 mTorr (10-20 sccm), at a wire temperature of approximately 2200 K. Under these conditions, a large flux of atomic H can be generated, and this species can effectively clean the chamber by etching amorphous silicon at rates up to 200 nm/min, as reported by Uchida *et al.*¹³

Threshold Ionization Mass Spectrometry Data Acquisition

The raw data obtained by this technique consists of a scan in masses (28-32 amu) at a fixed electron energy of 10.5 eV. To obtain the raw signal intensity for each species, the spectrum was integrated across a 1 AMU interval (e.g. 27.5 to 28.5 m/z for Si). A background scan was made with no SiH₄ present and the wire on, and this was subtracted from the raw data. Next, a scan was made with the gas present, but the wire off in order to assess the extent of dissociative ionization of SiH₄ at 10.5 eV, due to the finite electron energy distribution. In order to subtract this additional background contribution, a gas temperature correction was necessary as these data were acquired with the wire off. Comparing the signal intensity of Ar, with and without the wire on (and applying a mass correction factor since intensity \sim mass^{-1/2}), enabled the wire off data to be normalized and then subtracted from the raw data. Also, since the raw data at masses 29 and 30 includes not only the contribution from the SiH and SiH₂ radicals, but contributions from Si isotopes (²⁹Si: 4.7% abundance, ³⁰Si: 3.1% abundance), a correction was necessary to extract the radical contribution. Given the differing efficiencies with which the various radicals can be ionized (electron ionization cross sections), normalization of the background-corrected data is necessary to determine their relative abundance. The cross section for Si comes from the measurements by Freund *et al.*¹⁴ For the other SiH_x, cross section measurements by Tarnovsky *et al.*¹⁵ were used. After subtracting the background contributions to the raw data, the cross section normalization was applied. The sensitivity attainable with this technique is estimated to be better than 1 ppm, taking the ratio of the minimum distinguishable radical signal (of order 10⁻¹² Torr) to the total pressure (of order 10⁻⁶ Torr).

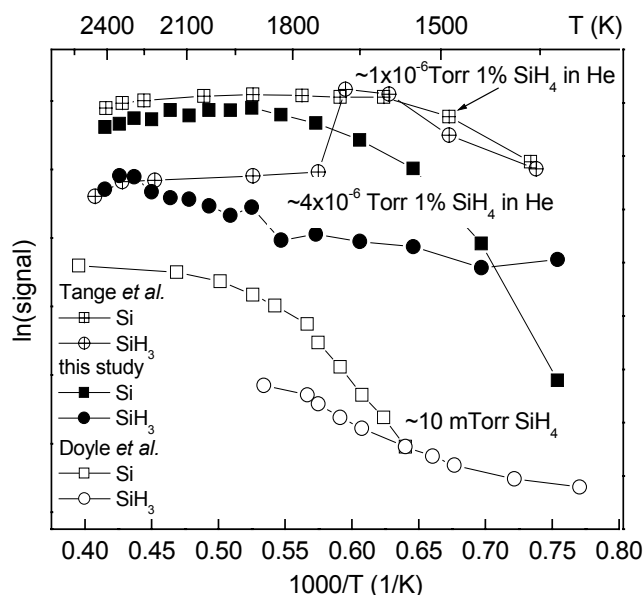


Figure 2. Low pressure (5×10^{-6} Torr) radical species measurements obtained using a new W wire. Activation energy accurate to within $\pm 10\%$, due to wire temperature uncertainties (± 50 K); error bars are not shown.

Results from Gas Species Detection

Radical Detection – new wire

The distribution of monosilicon radical species as a function of wire temperature (1300-2500 K), at a total pressure of 5×10^{-6} Torr, is shown in Figure 2. These results were obtained with a new wire having had no previous SiH_4 exposure. In order to be able to measure results for a

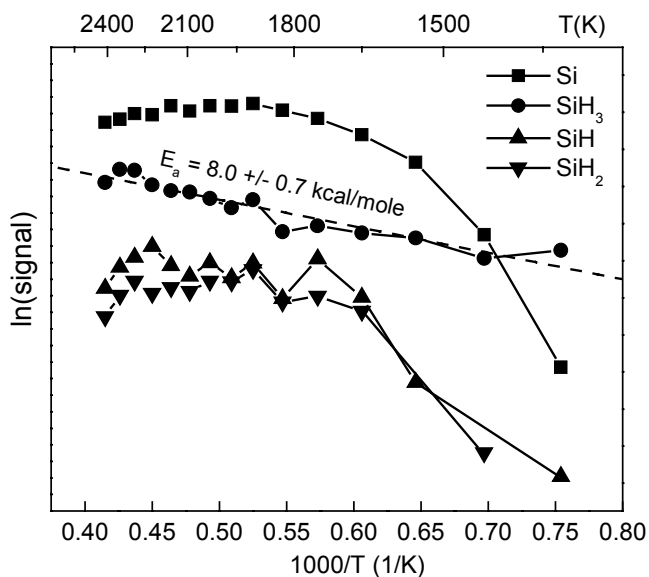


Figure 3. Summary of experimental studies on W wire surface kinetics.

bare wire without silicide formation, the highest temperature measurements were made first, and then the wire temperature was decreased in steps to 1300 K. Starting at the lowest temperatures, at which point a silicide or Si film forms,⁷ revealed a hysteresis in the Si signal, likely related to the desorption of this silicide or Si film from the wire. Figure 3 compares the results of this study to those of similar low pressure studies (also utilizing W wires).^{4,7} The only species shown in Figure 3 are Si and SiH₃, as they were the predominant species in the present study, as well as in that of Doyle *et al.*⁷ In the study of Tange *et al.*,⁴ the SiH₂ signal exhibited very similar characteristics as SiH₃ and thus is omitted for clarity. Similar to the other studies,^{4,5,7} we find that Si is the predominant radical desorbed from the wire for wire temperatures above 1500 K. Above 1800 K, a saturation in the Si signal is noted, with a slight decrease above 2300 K, an effect also observed in these studies. This phenomenon has been attributed to competition between desorption and decomposition;¹⁶ it should be pointed out that diffusion of Si through the wire may also be important at these high temperatures. The observation of primarily Si desorption at high temperatures indicates that surface decomposition of SiH₄ is faster than evaporation of SiH_x at these temperatures.

The second most abundant radical evident from Figure 2 is SiH₃, in agreement with the report by Doyle *et al.*⁷ Over the entire temperature range investigated (1300-2500 K), this radical signal shows a small activation energy of 8 kcal/mole, regardless of the condition of the wire surface. As the formation of this species is believed to involve an H atom exchange at the surface, such a small, constant activation energy is reasonable.⁷ Also suggested by this result is that SiH₃ formation is catalyzed as this activation energy is much smaller than the bond dissociation energy of SiH₄ (90 kcal/mole, Ref. 17). The radicals SiH and SiH₂ were detected in small quantities (<8% of Si), only slightly larger than the isotopic contributions from ²⁹Si (4.7%) and ³⁰Si (3.1%).

Radical Detection – aged wire

A recent study by Mahan *et al.*² focused on the effect of wire alloying on the electronic properties of hydrogenated amorphous silicon films. They suggested that the differences in film electronic properties observed were most likely related to differences in radical chemistries associated with a ‘virgin’ wire versus an alloyed wire. As a means of investigating whether there are discernable differences in radical chemistry depending on the condition of the wire, we have made low pressure radical measurements on aged wires to complement those performed on new wires. The temperature dependence of the SiH_x radical signals with the use of an aged wire (one used on several previous deposition runs, with SiH₄ partial pressures of order 10mTorr and temperatures of 2000°C) is shown in Figure 4. The primary differences in surface kinetics with the use of the aged wire are the observation of high temperature (>2100 K) activation energies for all radicals detected, as compared with the signals detected for a new wire, shown in Figure 2. In particular, the SiH₃ signal exhibits an activation energy of 106 kcal/mole, substantially higher than the 8 kcal/mole observed with a new wire, and close to the Si-H bond dissociation

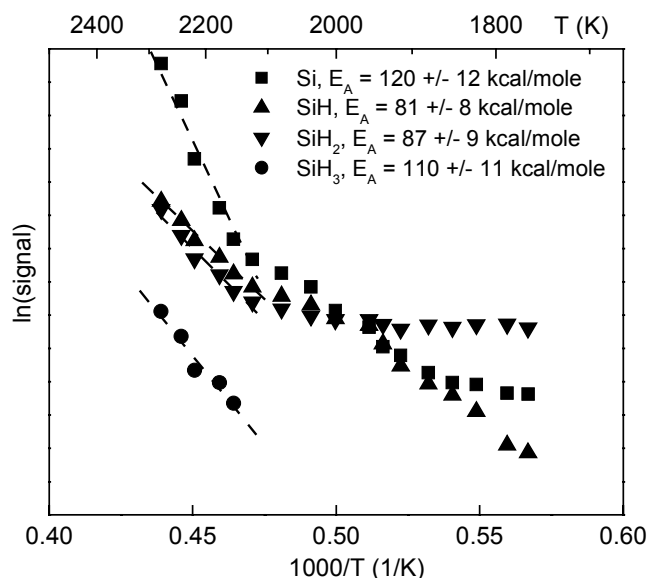


Figure 4. SiH_x radical signals measured from an aged W wire at a total pressure of 5×10^{-6} Torr. Activation energies quoted are accurate to within $\pm 10\%$, due to uncertainties ($\pm 50\text{K}$) in wire temperature; error bars are not shown.

energy of SiH_4 . This suggests that the aging of the wire has led to a reduction, if not an elimination, of its catalytic activity. It is also noteworthy that the high temperature activation energy measured for Si (117 kcal/mole) is close to the known heat of vaporization of liquid Si (92 kcal/mole), within experimental uncertainties. Also, in contrast to the results obtained with the new filament, SiH and SiH_2 are both in greater abundance than SiH_3 . The cause for this might be the contribution of heterogeneous pyrolysis to SiH_4 decomposition. At low pressures, surface-initiated SiH_4 pyrolysis (on the wire) should produce SiH_2 predominantly, while SiH_3 can be ruled out as a primary product, based on the enthalpy of its formation reaction.¹⁷ The lower formation enthalpy for SiH relative to SiH_3 , as determined by thermodynamic calculations,¹⁸ may also explain its greater relative abundance. However, it is clear that the amount of liquid Si remaining on the wire is large enough such that its evaporation dominates over pyrolysis of SiH_4 to other SiH_x .

Wire Characterization

Scanning Electron Microscopy

To complement radical measurements and gain insight into the nature of the changes occurring at the wire surface, *ex-situ* diagnostics were performed on portions of wires, including the aged wire referred to above. Field emission scanning electron microscopy (SEM), operating at 30.0 kV with 1.5 nm point resolution, was used to characterize the surface morphology of three different wires. Figure 5 depicts the SEM images of a new wire (with no previous SiH_4 or high temperature exposure), a heat-treated wire (having minimal SiH_4 exposure at the operating temperature of 2000°C for approximately 10 hours), and an aged wire (having had exposure to a partial pressure of 10mTorr SiH_4 at 2000°C for approximately 10 hours). Evident with the new wire are striations caused by the wire extrusion process, while the heat-treated wire appears to have a much smoother, glassy surface (it should be noted that the heat-treated wire also appears

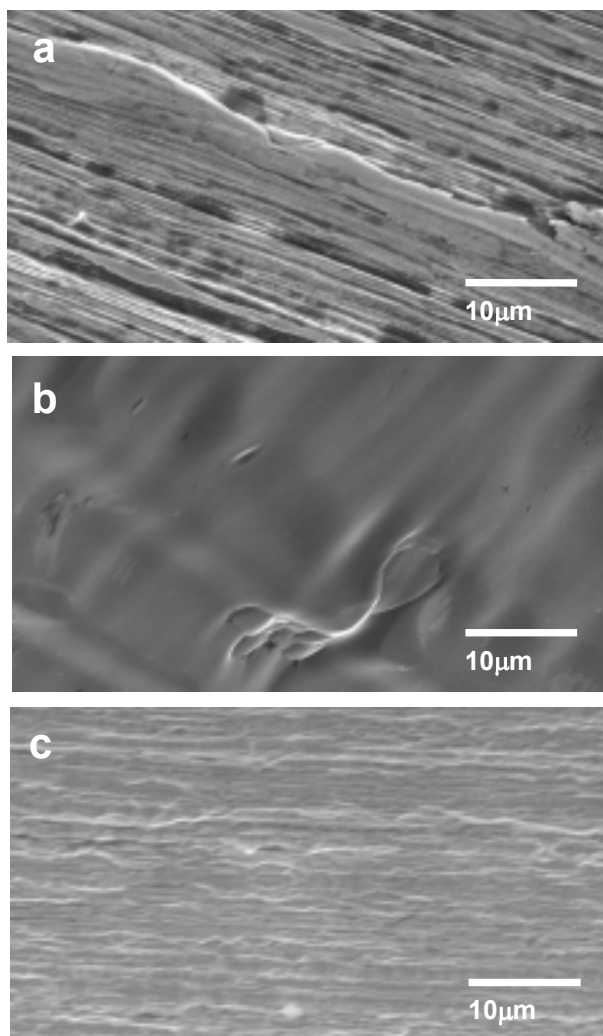


Figure 5. Surface morphology of new (a), heat-treated (b), and aged (c) wires.

to have a much higher reflectivity). The properties of the heat-treated wire could be a result self-diffusion of W along the wire surface that takes place at these high temperatures. The latter image of the aged wire reveals a much rougher, irregular surface with striation lines absent, similar to observations of Mahan *et al.*² for a comparably aged wire. Since the wires used during deposition go through the high temperature treatment before the introduction of SiH_4 , the surface morphology observed with the aged wire is attributed to deposition of Si (present as elemental Si and/or a silicide phase). Given the profound differences in surface morphology of the heat-treated and aged wire, it is not surprising that large differences in activation energies for radical desorption are observed.

Auger Electron Spectroscopy

To provide insight into the changes in chemical composition that occur during wire aging, Auger Electron Spectroscopy (AES) was used to probe discrete points at the wire surface and interior (having a spatial resolution of order $0.1\mu\text{m}$ and sampling depth of order 10 nm). Figure 6 is a low magnification SEM image of the aforementioned aged wire, revealing the locations at which AES measurements were made; the measured composition is given in Table 1. The ratio Si/(Si+W) is quoted as the other impurities detected (carbon, oxygen) were thought to be a result of *ex-situ* contamination. As a result, the ratio Si/(Si+W) should be representative of the overall fraction of Si in the wire during the high temperature exposure to SiH_4 in the chamber. As evident from Table 1, the Si concentration at the surface reaches as high as 15% and drops off precipitously to approximately 2% in the interior of the wire; surface concentrations at other locations ranged from that given by points “a” and “b” (11.6-15.1%). The two interior points “c” and “d” (5% and 2% Si, respectively) were estimated to be approximately $25\mu\text{m}$ and $50\mu\text{m}$ in depth. It is noteworthy that these concentrations are comparable to the equilibrium solid solubility of Si in W at the respective wire temperatures.

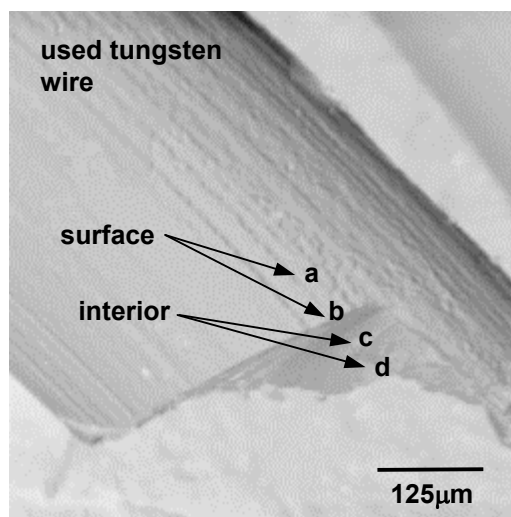


Figure 6. Scanning electron microscopy (SEM) image of aged tungsten wire.

Discussion

Examining the Si-W phase diagram in Figure 7 (generated with TAPP¹⁹), in light of these measured concentrations, shows that silicon concentrations of 15% at a typical wire temperature of 2000°C corresponds to a two-phase equilibrium between the silicide W_5Si_3 (33% abundance) and tungsten (67% abundance) at a silicon solubility of 4%. The Auger measurements support the idea that the nature of the wire alloying or aging process involves the growth of a silicide layer. Given that, at a depth of 10% of the wire radius ($25\mu\text{m}$), silicon is present only up to its

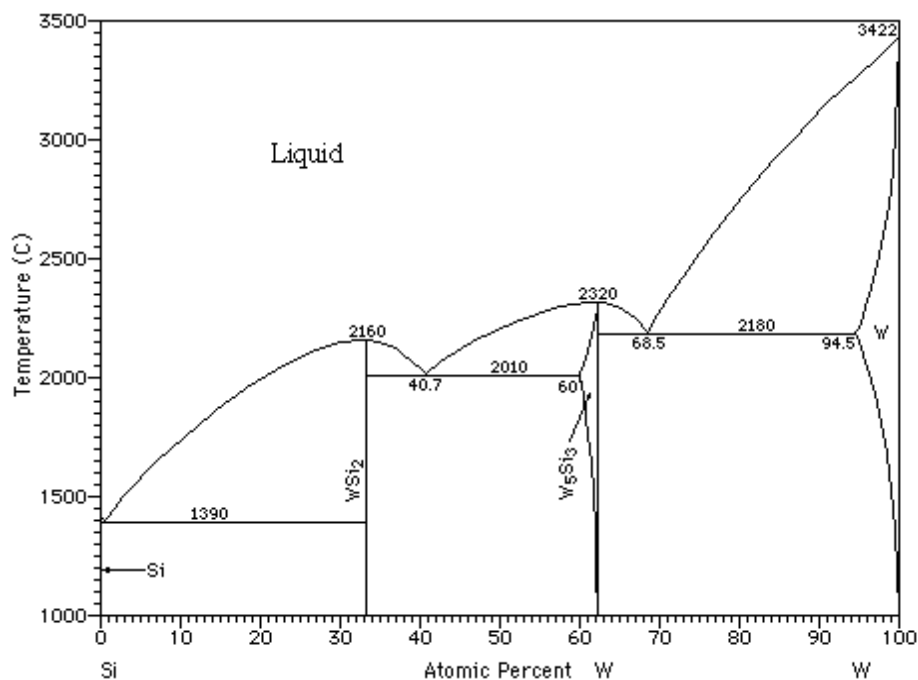


Figure 7. Si-W phase diagram, created with TAPP v2.1 (Thermochemical and Physical Properties), ES Microwave, 1991.

Table 1. Composition of used tungsten wire, as determined by Auger Electron Spectroscopy (AES).

Location	Si/(Si+W)
Surface (a)	11.6%
Surface (b)	15.1%
Interior (c) – 25 μ m deep	4.9%
Interior (d) – 50 μ m deep	1.9%

solubility limit, the silicide layer is likely to be thin. Under more severe conditions (larger Si concentrations at lower temperatures), the silicide constitutes a large fraction of the wire, as Figure 7 reveals. As the silicide is more brittle than elemental tungsten, this leads to the wire breakage so commonly observed in HWCVD reactors.

To provide some insight into the kinetics of Si diffusion into W, additional radical measurements were made. A standard aging treatment was adopted for these measurements, consisting of a 15 minute bake at $\sim 1000^{\circ}\text{C}$ in an ambient of SiH_4 at a partial pressure of 0.2 mTorr (20 mTorr total, balance He). A mass spectrum was then acquired at a higher wire temperature (1470°C), at a SiH_4 partial pressure of 4.4×10^{-8} Torr, followed by a scan in the absence of SiH_4 . Figure 8 reveals contributions from Si and SiH_3 (produced by H abstraction from SiH_4) for the case of the SiH_4 background. In the absence of SiH_4 , Si is the predominant radical observed, and this signal is attributed to Si (in excess of the thermodynamic solubility) diffusing from the interior of the wire; this signal was observed to persist for more than 1 hour, with no decrease in intensity. Comparing the relative magnitudes of the two signals, one estimates that the diffusion signal corresponds to a SiH_4 partial pressure of $\sim 2 \times 10^{-8}$ Torr (it should be noted that this contribution is relatively small compared to the SiH_4 partial pressures of >1 mTorr, typical of growth conditions). For an assumed average concentration of 1% Si throughout the entire wire, a simple calculation shows that the corresponding pressure would be ~ 30 mTorr, at a typical wire temperature of 1800°C . This result suggests that the time scale to completely deplete the wire of its Si is extremely long, consistent with the mass spectrometry observations suggesting Si diffusion.

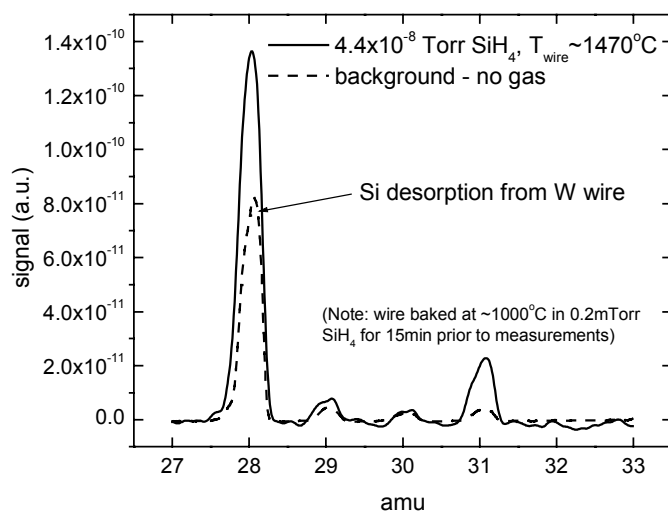


Figure 8. Mass spectrometry evidence for Si incorporation by W wire.

Rates for Surface Kinetic Processes

A comparison of the relative rates for the various surface kinetic processes, namely, diffusion, evaporation, and decomposition allows further insight into the nature of the wire aging process. At the highest temperatures investigated in this study (~2400 K), the solid solubility of Si in W is a few atomic percent, dropping to less than 1 at.% at the lowest temperature (1273 K). To our knowledge, there have been no studies that examined the diffusion of Si into elemental W. A study by Kharatyan *et al.*,²⁰ however, investigated the diffusion of Si into various silicides of tungsten and molybdenum. For the diffusion of Si into W_5Si_3 (the only silicide for which data were available), a diffusion coefficient of

$$D_{W_5Si_3}^{Si} = 6.9 \exp(-69000 \pm 5000 / RT), \text{cm}^2/\text{s} \quad (1)$$

was obtained.²⁰ Using this diffusion coefficient, the time scale for diffusion (using the wire radius as a lower limit for the characteristic length) as a function of wire temperature is given in Figure 9.

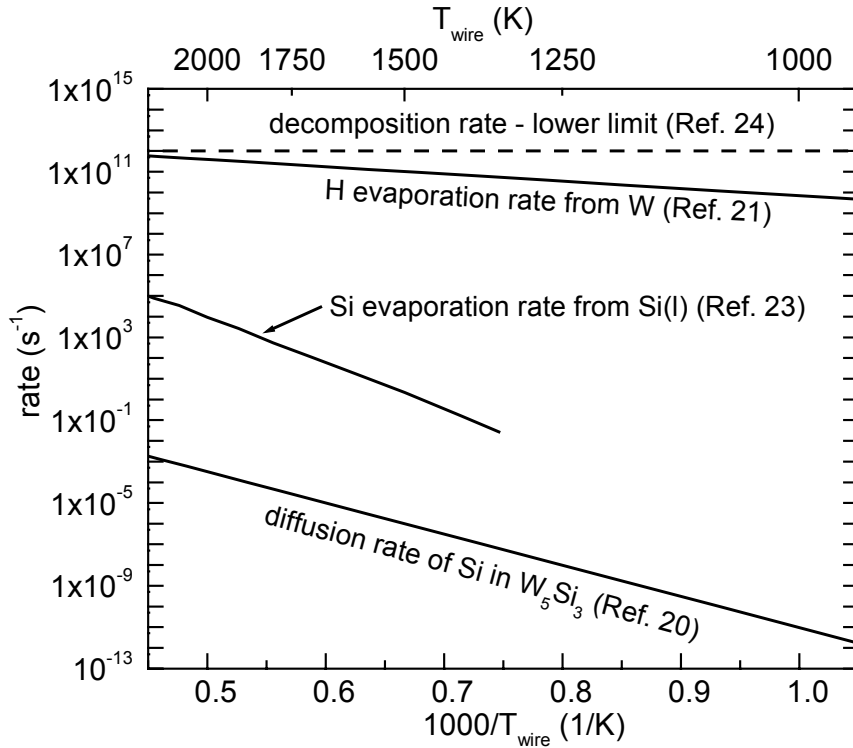


Figure 9. Rates of interest for wire surface kinetic processes.

Data on the evaporation rate of Si from W were unavailable, but the study by Ehrlich²¹ does provide an evaporation rate for H from W,²² which is relevant to the SiH_4 decomposition process; this rate is plotted in Figure 9. The evaporation rate of Si from liquid Si could be determined from the vapor pressure data of Margrave.²³ As liquid Si can form at some point during the aging process (Figure 7, $W < 33\%$ / $Si > 66\%$), this rate has relevance to the aged wires of this study. This rate of evaporation, as a function of wire temperature, is also plotted in Figure 9. Finally, rates of SiH_4 decomposition on W were not directly available, but a study by Yang *et al.*²⁴ suggests the time scale for Si-H bond breaking is of order a few picoseconds (in a

liquid environment), establishing a lower bound to the decomposition rate for the significantly higher temperatures in the present study; this rate is included for comparison in Figure 9.

Examining these rates in Figure 9, bulk diffusion of Si through the silicide is clearly the slowest process, followed by Si evaporation, and then decomposition. These rates, coupled with experimental observations, give a picture of the relative rates of surface kinetic processes on the wire. First, the high rate of decomposition compared with evaporation and diffusion suggests that for the vast majority of wire temperatures, Si (as opposed to other SiH_x) is the predominant evaporating/diffusing species; radical measurements in particular support the idea that it is the dominant evaporating species. Next, the Auger and radical measurements described earlier provide clear evidence that diffusion through the wire is occurring, and at rates faster than predicted by bulk diffusion alone. This suggests that the majority of Si that diffuses into the wire does so before a thick silicide has formed. Whether this higher *effective* diffusivity is due to a higher intrinsic rate of Si diffusion into W (rather than W_5Si_3) or diffusion occurring primarily through cracks that develop on the surface of the wire is unclear. Finally, it appears that the rate of evaporation of Si from Si(l) is several orders of magnitude below that of decomposition, even at the highest wire temperatures. It was previously observed, however, that for wire temperatures in excess of 2000 K, a saturation in the Si signal occurs with the use of a new wire that does not occur with an aged wire. This observation is consistent with a competition between evaporation and decomposition. This, in turn, suggests that the mechanism of Si desorption from a new wire does not consist of Si evaporation from Si(l), but a different mechanism, namely, the direct desorption of Si from a W surface. The rate for this process is likely to be of a similar magnitude as H evaporation from W, depicted in Figure 9.

A picture then emerges of the hot-wire CVD decomposition process. First, SiH_4 is adsorbed and then rapidly decomposed to Si and H on the surface of a new wire. This surface Si will then either evaporate or, if the surface concentration is high enough, diffuse to the interior of the wire up to its solubility limit. Once the thermodynamic solubility has been reached, excess Si can contribute to the formation of the W_5Si_3 phase, or at higher concentrations, WSi_2 . At the highest Si concentrations (>67%), liquid Si can form at the surface and then Si evaporation from Si(l) becomes the dominant mechanism of Si production. The observation that a new wire readily absorbs Si, but retains it for a long period of time can be explained as a silicide diffusion-limited process. The silicide that forms at the surface acts as a diffusion barrier to Si in the interior of the wire (as well as to further diffusion of surface Si into the wire), and Figure 9 shows that the characteristic diffusion time at the wire temperature used (~1750 K) is, at minimum, several hours.

Summary of Wire Surface Kinetics Studies

With the use of a new wire, Si is found to be the predominant radical produced in a HWCVD reactor for wire temperatures in excess of 1500 K. For temperatures below 1500 K, the SiH_3 radical becomes predominant. The small activation energy (8 kcal/mole) observed for SiH_3 formation suggests the process is catalyzed with the use of these wires. These results are in qualitative agreement with previous studies of radical chemistry at the wire. Radical measurements performed on aged wires show high temperature activation energies for all SiH_x species, suggesting a non-catalyzed process for radical formation.

Scanning electron microscopy of aged wires revealed a surface both rougher and more irregular than seen with new or heat-treated wires; this morphology is thought to be characteristic of Si deposition (either as free Si or a silicide). Auger electron spectroscopy

revealed surface Si concentrations as high as 15%, suggesting a two-phase equilibrium between W_5Si_3 and W (at a Si solubility of 4%). Concentrations of Si in the interior of the wire (2-5%) are of order the solubility limit and reveal that Si diffusion into the wire is significant. Radical measurements added further evidence of Si diffusion, as Si was detected in a silane-free ambient following an aging treatment.

Examining rates for various surface kinetic processes reveals that bulk diffusion of Si through a silicide is the slowest, followed by Si evaporation and then surface decomposition. The high rate of surface decomposition supports the idea that Si is in fact the predominant evaporating and diffusing species. In light of the low rate of diffusion through the silicide, the diffusion mechanism in the initial stages of SiH_4 exposure must either consist of bulk diffusion through elemental W or large cracks that develop on the wire surface and propagate to the interior of the wire. Finally, experimentally observed evaporation kinetics suggest that Si desorption from a new wire comes from direct Si-W bond breakage, as opposed to evaporation from Si(l).

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Publications Under Subcontract:

1. ***"Manipulation And Control Of Nucleation And Growth Kinetics With Hydrogen Dilution In Hot-Wire CVD Growth Of Poly-Si,"*** J. K. Holt, M. Swiatek, D. G. Goodwin, and Harry A. Atwater, Proceedings of Symposium A, Spring 2000 Materials Research Society Meeting, San Francisco, CA.
2. ***"Large-Grained Polycrystalline Si Films Obtained By Selective Nucleation And Solid Phase Epitaxy,"*** R. A. Puglisi, H. Tanabe, C. M. Chen, H. A. Atwater, Materials Science And Engineering B-Solid State Materials For Advanced Technology **73**: (1-3) 212-217 (2000).
3. ***"A Relation Between Surface Oxide And Oxygen-Defect Complexes In Solid-Phase Epitaxial Si Regrown From Ion-Beam-Amorphized Si Layers,"*** M. P. Petkov, C. M. Chen, H. A. Atwater, S. Rassiga, K. G. Lynn, Applied Physics Letters **76**: (11) 1410-1412 (2000).
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5. ***"Gas Phase And Surface Kinetic Processes In Polycrystalline Silicon Hot-Wire Chemical Vapor Deposition,"*** J.K. Holt, M. Swiatek, D.G. Goodwin, And H.A. Atwater, 1st International Conference on CAT-CVD (Hot-Wire CVD) Processes, Kanazawa, Japan.
6. ***"Si + SiH₄ Reactions And Implications For Hot-Wire CVD Of a-Si:H: Computational Studies,"*** R.P. Muller, J.K. Holt, D.G. Goodwin, And William A. Goddard, III, Spring 2000 Materials Research Society Meeting, San Francisco, CA.
7. ***"Gas Phase And Surface Kinetic Processes In Polycrystalline Silicon Hot-Wire Chemical Vapor Deposition,"*** J.K. Holt, M. Swiatek, D.G. Goodwin, R.P. Muller, W.A. Goddard III, and H.A. Atwater, *Thin Solid Films* **395**, 29-35 (2001).
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Ph.D. Theses under Subcontract:

1. “*Hot-Wire Chemical Vapor Deposition Of Silicon And Silicon Nitride For Photovoltaic Applications*”, Ph.D. Thesis By Jason Knowles Holt, California Institute Of Technology, Pasadena, California, 2002
2. “*Polycrystalline Silicon Thin Films for Photovoltaics*”, Ph.D. Thesis by Claudine Minnie Chen (Applied Physics and Environmental Engineering Science) California Institute of Technology, Pasadena, California, 2002

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